Different Pr$^{3+}$ environments in Pr$_{1.85}$Ce$_{0.15}$CuO$_4$: A Raman crystal-field excitation study

J. A. Sanjurjo, G. B. Martins, P. G. Pagliuso, E. Granado, I. Torriani, and C. Rettori

Instituto de Física “Gleb Wataghin,” Universidade Estadual de Campinas, 13083-970 Campinas, São Paulo, Brazil

S. Oseroff
San Diego State University, San Diego, California 92182

Z. Fisk
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Low-temperature Raman scattering of crystal-field (CF) excitations within the Pr$^{3+}$ ground-state $^2$H$_4$ multiplet of the compound Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ suggests the presence of more than one CF environment for the Pr$^{3+}$ ions. The Raman spectra were similar to spectra obtained in inelastic neutron-scattering experiments. The analysis of the Raman spectra for Pr$_{1.85}$R$_{0.15}$CuO$_4$ samples with R=Pr, La, Y, Ce, and Th indicates three different environments for Pr$^{3+}$. One is associated with charge transfer caused by the replacement of Pr$^{3+}$ by the tetravalent ions Ce$^{4+}$ or Th$^{4+}$. A second is almost identical to that observed in Pr$_2$CuO$_4$. The third is attributed to either an orthorhombic distortion or to sites of smaller lattice volume. The Nd- and Nd(Ce)-based compounds are also discussed.

I. INTRODUCTION

Crystal-field (CF) studies in high-temperature superconductors (HTS's) are extremely interesting, particularly for Ln$_2$CuO$_4$ (Ln = La, Pr, Nd) compounds, in which superconductivity is induced by a doping process. In the La-based compounds a divalent dopant (Sr$^{2+}$ or Ba$^{2+}$) oxidizes the CuO$_2$ planes, leaving holes as supercurrent carriers. In contrast, doping of the Nd- and Pr-based compounds with tetravalent Ce or Th reduces the

II. EXPERIMENTAL DETAILS

The Raman data were taken between 10 K and 293 K. The samples were platelike single crystals of Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ having their c axis perpendicular to the large face. The samples were not subjected to reducing thermal treatments; hence, all our measurements were taken in the normal state. The crystals were grown from a nominally stoichiometric mixture of the respective oxides, using PbO- and CuO-based fluxes in Pt crucibles. The Pb content was less than 10% of the recipe.
TABLE I. Refined values of lattice parameters (Å) for Pr$_{1.85}$R$_{0.15}$CuO$_4$ (R=Pr, La, Y, Ce, Th). The ionic radius (Å) is given beside each R.

<table>
<thead>
<tr>
<th></th>
<th>Pr$^{3+}$(1.09)</th>
<th>La$^{3+}$(1.15)</th>
<th>Y$^{3+}$(0.93)</th>
<th>Ce$^{4+}$(1.01)</th>
<th>Th$^{4+}$(0.95)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.959(1)</td>
<td>3.963(1)</td>
<td>3.954(1)</td>
<td>3.961(1)</td>
<td>3.967(1)</td>
</tr>
<tr>
<td>c</td>
<td>12.236(3)</td>
<td>12.257(3)</td>
<td>12.185(3)</td>
<td>12.193(3)</td>
<td>12.186(3)</td>
</tr>
</tbody>
</table>

three different samples of Pr$_{1.85}$Ce$_{0.15}$CuO$_4$. Similar spectra were obtained from different regions of the samples, and also for samples with lower nominal Ce concentrations (0.05 ≤ x ≤ 0.15). It is clearly seen that Ce doping broadens the spectra, developing multiple features in which at least three peaks may be identified. For XX and ZZ polarization the CF excitations are forbidden according to the selection rules of the Raman process. Figure 2 shows the Raman spectra of Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ for different polarizations. These data suggest that the multiple-peak structure observed for the ZZ polarization between 100 and 175 cm$^{-1}$ corresponds to the CF excitation between the ground state $\Gamma_4$ and the first excited $\Gamma_5$ state. Moreover, Figure 3 shows greater thermal broadening for the multiple-peak structure than for the A$_{1g}$ phonon mode, characteristic of faster relaxation for the CF excitations.

Figure 4 shows the Raman spectra for Pr$_{1.85}$R$_{0.15}$CuO$_4$ (R= La, Y, Ce, and Th) and Pr$_2$CuO$_4$ polycrystalline samples. The electron-doped (n-type) compounds (R= Ce$^{4+}$, Th$^{4+}$) show basically the same multiple-peak structure, but less resolved, as that observed in single crystals and attributed to CF excitations. In contrast, the undoped compounds (R= La$^{3+}$, Y$^{3+}$) show a single narrow peak at ~153 cm$^{-1}$ for La and a relatively broad peak at ~156 cm$^{-1}$ for Y. In both, this peak is very close to that observed in Pr$_2$CuO$_4$ at ~155 cm$^{-1}$.

IV. ANALYSIS AND DISCUSSIONS

In a recent letter on Raman experiments we showed that the CF excitations at 156, 540, and 690 cm$^{-1}$ (Ref. 16) in Pr$_2$CuO$_4$ were very close to the CF transitions observed in INS experiments. In this work as well, the multiple-peak structure observed between 100 and 175 cm$^{-1}$ for Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ (see Fig. 1) shows basically the same features observed in INS experiments for the same energy interval (12–22 meV). Thus, we conclude that the origin of the multiple-peak spectra is the same in both experiments and may be associated with the presence of Pr$^{3+}$ having different CF environments, coexisting within the area of the focusing laser spot (~100 µm diam.). But we should mention that while the INS experiment showed two nearly resolved peaks at ~653 and ~710 cm$^{-1}$ for the Ce$^{4+}$-doped compound, our Raman experiments failed to detect these transitions.

Figure 5 shows, for the most highly resolved Raman spectra of Fig. 1(a), that the spectrum is equally well simulated by the superposition of either three or four Lorentzian lines having the appropriate energy positions, linewidths, and relative intensities. The simulations and calculated parameters are shown in the figure. Similar simulations were carried out for the spectra shown in Figs. 1(b) and 1(c) with approximately the same parameters.

It is thus clear that the multiple-peak structure observed in the Raman spectra for the Ce- and Th-based compounds may be associated with the presence of three different Pr$^{3+}$ environments. The peak at ~151 cm$^{-1}$ could be attributed to a Pr$^{3+}$ site (site I) having an environment slightly perturbed from that in the pure compound Pr$_2$CuO$_4$ (see Fig. 1). This is supported by the nearly identical lattice parameters and Raman spectra.
leads to a stronger local crystal electric field. The first excited $\Gamma_5$ CF level may then shift toward higher energy, giving rise to a single line at $\sim 163$ cm$^{-1}$ [see Fig. 5(a)]. Second, Furusawa and Koyama$^{17}$ observed in a transmission electron diffraction experiment the presence of an orthorhombic phase in Pr$_{2-x}$Ce$_x$CuO$_4$. This would split the first excited $\Gamma_5$ CF level of Pr$^{3+}$, and the shoulder observed at $\sim 163$ cm$^{-1}$ could then be attributed to the high-energy component of the split line, as shown in Fig. 5(b).

In order to account for these different possibilities we adopted the CF analysis (without molecular field), given in Ref. 9. The Hamiltonian describing the crystal field can be written

$$H_{CF} = \sum_{k,q} B^k_q C^k_q,$$

(1)

where $C^k_q$ is the qth component of a spherical tensor of rank $k$, and the $B^k_q$ are the corresponding CF para.
TABLE II. Pr$^{3+}$ crystal-field parameters $B^+_n$ (meV) in Pr$_{2-x}$Ce$_x$CuO$_4$ ($x=0.0$, 0.15).

<table>
<thead>
<tr>
<th></th>
<th>Pr$_2$CuO$_4$</th>
<th>Pr$<em>{1.85}$Ce$</em>{0.15}$CuO$_4$</th>
</tr>
</thead>
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<tr>
<td>$B^+_1$</td>
<td>INS$^a$</td>
<td>Raman$^b$</td>
</tr>
<tr>
<td>$B^+_2$</td>
<td>-28</td>
<td>-30</td>
</tr>
<tr>
<td>$B^+_3$</td>
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<td>0</td>
</tr>
<tr>
<td>$B^+_4$</td>
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<td>-275</td>
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<tr>
<td>$B^+_5$</td>
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<td>21</td>
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<tr>
<td>$B^+_6$</td>
<td>228</td>
<td>228</td>
</tr>
<tr>
<td>$B^+_7$</td>
<td>224</td>
<td>224</td>
</tr>
</tbody>
</table>

$^a$From Ref. 9.  
$^b$From Ref. 13.

obtained from INS experiments.$^9$

Starting with the parameters obtained from the Raman$^b$ measurements of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$.$^9$ We now comment on the INS experiments in Pr$_{2-x}$Ce$_x$CuO$_4$. The INS spectra show broad...
duce a shift of the first $\Gamma_5$ excited state of Pr$^{3+}$ from $\sim$155 to $\sim$124 cm$^{-1}$ (see Fig. 6). A similar relative change of the CF parameters for Nd$^{3+}$ results also in a shift of the first $\Gamma_7$ excited state from $\sim$116 to $\sim$71 cm$^{-1}$. This agrees with the observation of a first excited level at $\sim$92 cm$^{-1}$ (11.5 meV) in INS experiments in Nd$_{1.85}$Ce$_{0.15}$CuO$_4$.$^{5,9,11}$

Loong and Soderholm$^{10}$ analyzed their INS data for Pr$_2$CuO$_4$ and report a different set of CF parameters and level scheme for the Pr$^{3+}$ ground state $3h_4$. They attribute the 710 cm$^{-1}$ peak, observed in Raman experiments at $\sim$690 cm$^{-1}$, to a transition between a $\Gamma_3$ ground state and a $\Gamma_4$ excited state. However, the Raman selection rules for a CF excitation between these two levels forbid this transition. Rather, for the level scheme given in Fig. 6, this peak is associated with a transition between the $\Gamma_4$ ground state and the $\Gamma_5$ and $\Gamma_2$ excited states, allowed by the Raman selection rules.$^{13}$ Furthermore, Loong and Soderholm$^{10}$ found a broad single peak for the first CF excitation in Pr$_{1.85}$Ce$_{0.15}$CuO$_4$, contrary to the multiple structure observed by us and Refs. 9 and 11.

Recently Martins et al.$^{20}$ measured electron spin resonance (ESR) of Gd$^{3+}$ in Pr$_{2-x}$Ce$_x$CuO$_4$ and found that the second-order $|b_{2i}|$ CF parameter of Gd$^{3+}$ decreases by about 23% upon doping. We therefore expect a similar reduction in the second-order $|B_{2i}|$ CF parameter of Pr$^{3+}$. $^{21}$ It is interesting to note that the absolute value of a second-order CF parameter weighted among different sites, $\langle B_{2i}^2 \rangle = \sum (I/I_0)B_{2i}^2$, where $i$ ranges over the various sites, gives $|B_{2i}^2| \simeq 23-25$ meV. This is about 22% smaller than the value for Pr$_2$CuO$_4$, in good agreement with the ESR results, though Gd$^{3+}$ has an $S$ ground state for which CF effects are observed only via spin-orbit coupling with the excited states.

V. CONCLUSIONS

In summary, we have shown that in as-grown Pr$_{1.85}$Ce$_{0.15}$CuO$_4$, there is more than one CF environment for the Pr$^{3+}$ ion. The CF excitation spectra observed in Raman and INS experiments for the electron-doped Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ compound can be interpreted in terms of three different Pr$^{3+}$ CF environments. The CF parameters for these sites describe well the observed Raman and INS spectra; however, as they were obtained in a simple way, they should be used with caution. One of these sites may be attributed to charge transfer associated with the doping process. Calculations from first principles will be needed in order to estimate the amount and localization of charge transfer that would account for the change in the CF parameters.

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16In Ref. 12 there is a misprint; the peak at 675 cm$^{-1}$ should read 690 cm$^{-1}$.